

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **SONY CORP**

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(72)Inventor : **SHIBUYA MASHIO
HATASAWA TAKENOBU
HARA TOMITARO
SHIBAMOTO GORO
GOTO SHUJI**

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(54) GEL PHASE ELECTROLYTE AND GEL PHASE ELECTROLYTE CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide gel phase electrolyte having good chemical stability to negative electrode, strength, and liquid maintaining property, and to provide a gel phase electrolyte cell having a large capacity, cycle property, load property, low temperature property by using the gel phase electrolyte.

SOLUTION: The nonaqueous electrolyte in which lithium containing solvent electrolyte salt is dissolved in the nonaqueous solvent and is formed is gel phase with matrix polymer to contain derivative of vinylene carbonate or vinylene carbonate in a range of 0.05 wt. %-5 wt. % with respect to the nonaqueous electrolyte.

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CLAIMS

[Claim(s)]

[Claim 1] The gel electrolyte with which the nonaqueous electrolyte which comes to dissolve a lithium content electrolyte salt in a non-aqueous solvent is the gel electrolyte which a matrix polymer comes to make into gel, and is characterized by containing the derivative of vinylene carbonate or vinylene carbonate to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range.

[Claim 2] The above-mentioned non-aqueous solvent is a gel electrolyte according to claim 1 characterized by ethylene carbonate and propylene carbonate being the mixed solvents which it comes to mix in 15:85-75:25 by the weight ratio.

[Claim 3] The gel electrolyte according to claim 1 characterized by containing LiPF₆, LiBF₄, LiN (CF₃SO₂)₂, or LiN (C₂F₅SO₂)₂ at least, and containing the above-mentioned lithium content electrolyte salt as the above-mentioned lithium content electrolyte salt so that the lithium ion concentration to the above-mentioned non-aqueous solvent may serve as the range of 0.4 or more mol/kg and 1.0 mol/kg or less.

[Claim 4] The gel electrolyte according to claim 1 characterized by using the polymer which repeats at least one kind in polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, a polyacrylonitrile, and the poly methacrylonitrile, and is included in a unit as the above-mentioned matrix polymer.

[Claim 5] The gel electrolyte according to claim 4 characterized by containing the copolymer with which it comes to carry out copolymerization of the hexafluoropropylene to polyvinylidene fluoride or polyvinylidene fluoride at 7.5% or less of a rate as the above-mentioned matrix polymer.

[Claim 6] The gel electrolyte according to claim 1 characterized by adding the difluoro anisole in the above-mentioned nonaqueous electrolyte in 0.2 % of the weight or more and 2% of the weight or less of the range.

[Claim 7] The negative electrode which has either of the carbon materials in which a

dope and a dedope of a lithium metal, a lithium alloy, or a lithium are possible, The positive electrode which has the multiple oxide of a lithium and transition metals, and the above-mentioned negative electrode and the above-mentioned positive electrode are intervened, and it has a gel electrolyte. The above-mentioned gel electrolyte While a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve a lithium content electrolyte salt in a non-aqueous solvent The gel electrolyte cell characterized by containing the derivative of vinylene carbonate or vinylene carbonate to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range.

[Claim 8] The above-mentioned non-aqueous solvent is a gel electrolyte cell according to claim 7 characterized by ethylene carbonate and propylene carbonate being the mixed solvents which it comes to mix in 15:85-75:25 by the weight ratio.

[Claim 9] The gel electrolyte cell according to claim 7 characterized by containing LiPF_6 , LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ at least, and containing the above-mentioned lithium content electrolyte salt as the above-mentioned lithium content electrolyte salt so that the lithium ion concentration to the above-mentioned non-aqueous solvent may serve as the range of 0.4 or more mol/kg and 1.0 mol/kg or less.

[Claim 10] The gel electrolyte cell according to claim 7 characterized by using the polymer which repeats at least one kind in polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, a polyacrylonitrile, and the poly methacrylonitrile, and is included in a unit as the above-mentioned matrix polymer.

[Claim 11] The gel electrolyte cell according to claim 10 characterized by containing the copolymer with which it comes to carry out copolymerization of the hexafluoropropylene to polyvinylidene fluoride or polyvinylidene fluoride at 7.5% or less of a rate as the above-mentioned matrix polymer.

[Claim 12] The gel electrolyte cell according to claim 7 characterized by adding the difluoro anisole in the above-mentioned nonaqueous electrolyte in 0.2 % of the weight or more and 2% of the weight or less of the range.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the gel electrolyte with which a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve a lithium content electrolyte salt in a non-aqueous solvent, and the gel electrolyte cell using it.

[0002]

[Description of the Prior Art] As a power source of pocket mold electronic equipment, an industry top cell is occupying an important location. Because of small lightweight-ized implementation of a device, a cell is light, and using the storage space in a device efficiently is called for. To this, a lithium cell with large energy density and output density is the most proper.

[0003] a cell with a high configuration degree of freedom flexible also in it or the sheet

mold cell of a thin large area, and a thin shape -- a facet -- although a card mold cell of a product is desired, it is difficult to make the cell of a thin large area from the technique of using for sheathing the metal can used conventionally.

[0004] In order to solve this, the cell using an organic and inorganic solid electrolyte and the gel electrolyte using polymer gel is examined. Since an electrolyte is fixed, electrolytic thickness is fixed, and these cells have adhesive strength between an electrode and an electrolyte, and can hold contact. For this reason, it is not necessary to shut up the electrolytic solution by metal sheathing, or to put a pressure on a cell component. Therefore, film-like sheathing can be used and it becomes possible to make a cell thinly.

[0005] The electrolyte of all solid-states has small ion conductivity, and since the utilization to a cell is still difficult, the gel electrolyte is seen as a hopeful. It is possible to use the multilayer film which consists of poly membrane metallurgy group thin films etc. as sheathing. Especially the dampproof multilayer film that consists of a thermal melting arrival resin layer and a metallic foil layer is excellent in that sealing structure is easily realizable with a hot seal, the reinforcement of the multilayer film itself, or airtightness, and promising as a candidate of a sheathing material also from it is lightweight, is thin and cheaper than metal sheathing.

[0006]

[Problem(s) to be Solved by the Invention] However, unless the non-aqueous solvent in a gel electrolyte is a solvent with a matrix polymer and compatibility, it does not constitute a gel electrolyte. Moreover, when a film was used for cell sheathing, the solvent of a low-boiling point was used and a cell sets under hot environments, there is a possibility of the internal pressure of a cell increasing by the rise of the vapor pressure of the solvent, and producing bulging. Therefore, selection of a solvent has a limit.

[0007] Since the congealing point is high and the low-boiling point solvent used for the lithium ion battery, for example, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, etc. have low viscosity, it is very effective in raising the ion conductivity in electrolytic low temperature, but as mentioned above, the gel electrolyte cell which uses a multilayer film for sheathing cannot use these so much because of constraint of the solvent selection by compatibility or the boiling point.

[0008] Ethylene carbonate, propylene carbonate, etc. are available as matter which does not carry out a decomposition reaction to which the boiling point spoils the cell engine performance highly as a solvent of the gel electrolyte for cells. Furthermore, we developed the copolymer with the polyvinylidene fluoride to which copolymerization of the hexafluoropropylene was carried out in 7.5% or less of range by the weight ratio as a matrix polymer which was excellent in such solvents and compatibility and was excellent in chemical stability, the reinforcement of gel, and solution retention.

[0009] Moreover, when mixing and using ethylene carbonate and propylene carbonate as a non-aqueous solvent, if there is much propylene carbonate, a low-temperature property and a load characteristic will become good, but since first time charge-and-discharge effectiveness is bad, cell capacity is small and a cycle property also gets worse. Therefore, it was difficult to make the gel electrolyte cell excellent in cell capacity, cycle properties, load characteristics, and all the low-temperature properties.

[0010] This invention is proposed in view of the conventional actual condition which was mentioned above, and aims at offering the gel electrolyte cell on which cell capacity, the

cycle property, the load characteristic, and the low-temperature property were satisfied by using the gel electrolyte excellent in chemical stability, reinforcement, and solution retention, and its gel electrolyte.

[0011]

[Means for Solving the Problem] The gel electrolyte of this invention is characterized by containing the derivative of vinylene carbonate or vinylene carbonate to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range while a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve a lithium content electrolyte salt in a non-aqueous solvent.

[0012] In the gel electrolyte concerning this invention which was mentioned above, since the derivative of vinylene carbonate or vinylene carbonate is contained to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range, it becomes a negative electrode and the thing excellent in the chemical stability of a gel electrolyte. And as for the gel electrolyte cell using this gel electrolyte, first time charge-and-discharge effectiveness and capacity have been improved.

[0013] Moreover, the gel electrolyte cell of this invention intervenes the negative electrode which has either of the carbon materials in which a dope and a dedope of a lithium metal, a lithium alloy, or a lithium are possible, the positive electrode which has the multiple oxide of a lithium and transition metals, and the above-mentioned negative electrode and the above-mentioned positive electrode, and is equipped with a gel electrolyte. And the gel electrolyte cell of this invention is characterized by containing the derivative of vinylene carbonate or vinylene carbonate to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range while a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve the above-mentioned gel electrolyte a lithium content electrolyte salt in a non-aqueous solvent.

[0014] By the gel electrolyte cell concerning this invention which was mentioned above, since the above-mentioned gel electrolyte contains the derivative of vinylene carbonate or vinylene carbonate to the above-mentioned nonaqueous electrolyte in 0.05 % of the weight or more and 5% of the weight or less of the range, the above-mentioned gel electrolyte becomes the thing excellent in chemical stability with a negative electrode. And the gel electrolyte cell of this invention using such a gel electrolyte satisfies the outstanding first time charge-and-discharge effectiveness and cell capacity. There is depressor effect of bulging not only by it but the generation of gas, and change of the dimension configuration of a cell can be prevented.

[0015]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0016] The example of 1 configuration of the gel electrolyte cell concerning the gestalt of this operation is shown in drawing 1 thru/or drawing 3 . This gel electrolyte cell 1 is equipped with the gel electrolyte layer 4 allotted between the band-like positive electrode 2, the band-like negative electrode 3 which countered with the positive electrode 2 and was arranged, and a positive electrode 2 and a negative electrode 3 as shown in drawing 3 . And this gel electrolyte cell 1 is covered with the sheathing film 6 with which the

electrode winding object 5 shown in drawing 2 and drawing 3 which were wound around the longitudinal direction consists of an insulating material, and is sealed while the laminating of a positive electrode 2 and the negative electrode 3 is carried out through the gel electrolyte layer 4. And the positive-electrode terminal 7 is connected to a positive electrode 2, the negative-electrode terminal 8 is connected to the negative electrode 3, respectively, and these positive-electrode terminals 7 and negative-electrode terminals 8 are put between the obturation section which is the periphery section of the sheathing film 6.

[0017] The positive-active-material layer in which a positive electrode 2 contains positive active material is formed on both sides of a positive-electrode charge collector. As this positive-electrode charge collector, metallic foils, such as aluminium foil, are used, for example.

[0018] a positive-active-material layer -- first -- for example, positive active material, electric conduction material, and binding material -- homogeneity -- mixing -- a positive electrode -- a mixture -- carrying out -- this positive electrode -- a mixture is distributed in a solvent and it is made the shape of a slurry. Next, this slurry is applied to homogeneity on a positive-electrode charge collector with a doctor blade method etc., and it is formed by making it dry at an elevated temperature and flying a solvent. Here, the mixing ratio is not asked that what is necessary is just to distribute positive active material, electric conduction material, binding material, and a solvent to homogeneity.

[0019] Here, the multiple oxide of a lithium and transition metals is used as positive active material. Concretely, as positive active material, LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiAlO_2 grade are illustrated. One kind of not only use but two or more kinds of use is possible for a transition-metals element. $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ grade are mentioned as the example.

[0020] Moreover, as electric conduction material, a carbon material etc. is used, for example. Moreover, as binding material, polyvinylidene fluoride etc. is used, for example. Moreover, as a solvent, N-methyl pyrrolidone etc. is used, for example.

[0021] Moreover, the positive electrode 2 has the positive-electrode terminal 7 connected to the other end of the die-length direction by spot welding or ultrasonic welding.

Although this positive-electrode terminal 7 has the desirable thing of the shape of a metallic foil and a mesh, if a flow can be taken, even if it will be chemically [electrochemically and] stable and will not be a metal, it is satisfactory. As an ingredient of the positive-electrode terminal 7, aluminum etc. is mentioned, for example.

[0022] Although it is desirable to have come out in the same direction as the negative-electrode terminal 8, if a short circuit etc. does not take place and a problem does not arise in the cell engine performance, either, although in which direction the positive-electrode terminal 7 has come out, it is satisfactory. Moreover, if the connection place of the positive-electrode terminal 7 has taken electric contact, the location to attach and the approach of attaching will not be restricted to the above-mentioned example.

[0023] Moreover, the negative-electrode active material layer in which a negative electrode 3 contains a negative-electrode active material is formed on both sides of a negative-electrode charge collector. As this negative-electrode charge collector, metallic foils, such as copper foil, are used, for example.

[0024] a negative-electrode active material layer -- first -- for example, a negative-electrode active material and the need -- responding -- electric conduction material and

binding material -- homogeneity -- mixing -- a negative electrode -- a mixture -- carrying out -- this negative electrode -- a mixture is distributed in a solvent and it is made the shape of a slurry. Next, this slurry is applied to homogeneity on a negative-electrode charge collector with a doctor blade method etc., and it is formed by making it dry at an elevated temperature and flying a solvent. Here, the mixing ratio is not asked that what is necessary is just to distribute a negative-electrode active material, electric conduction material, binding material, and a solvent to homogeneity.

[0025] As a negative-electrode active material, the carbon material in which a dope and a dedope of a lithium metal, a lithium alloy, or a lithium are possible is used. Concretely, as a carbon material in which a dope and a dedope of a lithium are possible, graphite, difficulty graphitized carbon, easily graphitized carbon, etc. are mentioned.

[0026] Moreover, as electric conduction material, a carbon material etc. is used, for example. Moreover, as binding material, polyvinylidene fluoride etc. is used, for example. Moreover, as a solvent, N-methyl pyrrolidone etc. is used, for example.

[0027] Moreover, the negative electrode 3 has the negative-electrode terminal 8 connected to the other end of the die-length direction by spot welding or ultrasonic welding. Although this negative-electrode terminal 8 has the desirable thing of the shape of a metallic foil and a mesh, if a flow can be taken, even if it will be chemically [electrochemically and] stable and will not be a metal, it is satisfactory. As an ingredient of the negative-electrode terminal 8, copper, nickel, etc. are mentioned, for example.

[0028] Although it is desirable to have come out in the same direction as the positive-electrode terminal 7, if a short circuit etc. does not take place and a problem does not arise in the cell engine performance, either, although in which direction the negative-electrode terminal 8 has come out, it is satisfactory. Moreover, if the connection place of the negative-electrode terminal 8 has taken electric contact, the location to attach and the approach of attaching will not be restricted to the above-mentioned example.

[0029] A gel electrolyte contains a non-aqueous solvent, an electrolyte salt, and a matrix polymer. Moreover, by the gel electrolyte cell 1 of this invention, vinylene carbonate or its derivative is added in the gel electrolyte so that it may mention later.

[0030] As a non-aqueous solvent, the well-known solvent used as a non-aqueous solvent of nonaqueous electrolyte can be used. Specifically, the solvent which permuted the hydrogen of ethylene carbonate, propylene carbonate, gamma-butyrolactone, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dipropyl carbonate, ethyl propyl carbonate, or these carbonates by the halogen is mentioned.

[0031] These solvents may use one kind independently and may mix two or more sorts by predetermined presentation. It is desirable that ethylene carbonate and propylene carbonate use the mixed solvent which it comes to mix in 15:85-75:25 by the weight ratio also especially in it. When the low-temperature property of the gel electrolyte cell 1 will be spoiled if there is too more ethylene carbonate than this, and there is too much propylene carbonate, first time charge-and-discharge effectiveness, cell capacity, and a cycle property become less good.

[0032] As an electrolyte salt, what is dissolved in the above-mentioned non-aqueous solvent can be used. Alkali-metal ion, such as a lithium, and alkaline-earth-metal ion are mentioned to a cation. Moreover, as an anion, BF_4^- , PF_6^- , CF_3SO_3^- , $2(\text{CF}_3\text{SO}_2)\text{N}^-$, $2(\text{C}_2\text{F}_5\text{SO}_2)\text{N}^-$, etc. are mentioned. And the electrolyte salt obtained combining these cations and anions is used. As an electrolyte salt used, LiPF_6 , LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$,

LiN (C₂F₅SO₂)₂, and LiClO₄ grade are mentioned, for example.

[0033] In addition, although it is satisfactory if it is the concentration which can be dissolved in the above-mentioned solvent as electrolyte salt concentration, it is desirable that the range of lithium ion concentration is 0.4 or more mol/kg and 1.0 mol/kg or less to a non-aqueous solvent. If lithium ion salt concentration exceeds 1.0 mol/kg, the low-temperature property and cycle property of the gel electrolyte cell 1 will be degraded. Moreover, sufficient capacity is not securable if lithium ion concentration is thinner than 0.4 mol/kg.

[0034] And a matrix polymer gels the nonaqueous electrolyte which comes to dissolve the above-mentioned electrolyte salt in the above-mentioned non-aqueous solvent. The polymer which repeats polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, a polyacrylonitrile, and the poly methacrylonitrile, and is included in a unit as such a matrix polymer is mentioned. Such a polymer may use independently, two or more kinds may be mixed and one kind may be used for it.

[0035] It is desirable also especially in it to use the copolymer with which hexafluoropropylene was introduced into polyvinylidene fluoride or polyvinylidene fluoride at 7.5% or less of a rate as a matrix polymer. The range of number average molecular weight is 500,000-700,000, or the range of weight average molecular weight is 210,000-310,000, and, as for such a polymer, let intrinsic viscosity be the range of 1.7-2.1.

[0036] The sheathing film 6 carries out the sealing pack of the electrode winding object 5 which it comes to wind around a longitudinal direction while the laminating of a positive electrode 2 and the negative electrode 3 is carried out through the gel electrolyte layer 4. This sheathing film consists of dampproofing into which aluminium foil was inserted with the resin film of a pair, and an insulating multilayer film.

[0037] And vinylene carbonate or its derivative is added by the gel electrolyte by the gel electrolyte cell concerning this invention. By adding vinylene carbonate or its derivative, the chemical stability to the negative electrode of the gel electrolyte concerned can be raised to a gel electrolyte. And by using the gel electrolyte excellent in the chemical stability to a negative electrode, the first time charge-and-discharge effectiveness of the gel electrolyte cell 1 can be improved, and a high cell capacity can be obtained.

[0038] Moreover, as mentioned above, a gel electrolyte cell is one of the advantages with the ability of a lightweight multilayer film to be used [big] for sheathing. However, like [in the case of a rechargeable lithium-ion battery], when gas occurred by decomposition of a non-aqueous solvent etc. at the time of first time charge, there was a big problem that a cell will swell, by the gel electrolyte cell which used the multilayer film for sheathing.

[0039] this invention person found out that the generation of gas accompanying charge was controlled and expansion of a cell could be prevented by adding vinylene carbonate or its derivative to a gel electrolyte besides effectiveness which was mentioned above.

[0040] It is desirable to consider as 0.05 % of the weight or more and 5% of the weight or less of the range to the solvent in a gel electrolyte as an addition of vinylene carbonate or its derivative. If there are few additions of vinylene carbonate than 0.05 % of the weight, the effectiveness of raising charge-and-discharge effectiveness is not fully acquired, but neither a high cell capacity nor first time charge-and-discharge effectiveness can be acquired. Moreover, if the addition of vinylene carbonate exceeds 5 % of the weight, the discharge property in low temperature will fall on the contrary.

[0041] Therefore, by making the addition of vinylene carbonate or its derivative into 0.05 % of the weight or more and 5% of the weight or less of the range to the solvent in a gel electrolyte, without reducing the discharge property in low temperature, charge-and-discharge effectiveness can be raised and a high cell capacity and a cycle property can be acquired. Furthermore, the addition of more desirable vinylene carbonate or its derivative is 0.5 % of the weight or more and 3% of the weight or less of the range to the solvent in a gel electrolyte. A property which was mentioned above can be raised more by making the addition of vinylene carbonate into 0.5 % of the weight or more and 3% of the weight or less of the range to the solvent in a gel electrolyte.

[0042] Furthermore, it is desirable that the difluoro anisole (DFA) is added in the nonaqueous electrolyte which constitutes this gel electrolyte. In nonaqueous electrolyte, by adding a difluoro anisole, the charge-and-discharge effectiveness of the gel electrolyte cell 1 can be raised, and a high discharge capacity can be obtained. It is desirable to consider as 0.2 % of the weight or more and 2% of the weight or less of the range to nonaqueous electrolyte as an addition of a difluoro anisole.

[0043] Since vinylene carbonate or its derivative is added by the gel electrolyte, the first time charge-and-discharge effectiveness of the gel electrolyte cell 1 of this invention which has a configuration which was mentioned above of a cell improves, it becomes what has a high cell capacity, and turns into a cell which was further excellent also in the cycle property. Moreover, since the generation of gas accompanying charge and discharge is controlled, even if the gel electrolyte cell 1 of this invention by which vinylene carbonate or its derivative is added by the gel electrolyte uses a multilayer film for sheathing, it does not have expansion of a cell, and becomes what has high dependability.

[0044] In addition, in the gel electrolyte cell 1, it is desirable that the piece 9 of resin is allotted to the contact part with the sheathing film 6, the positive-electrode terminal 7, and the negative-electrode terminal 8 as shown in drawing 1 thru/or drawing 3 . By allotting the piece 9 of resin to a contact part with the sheathing film 6, the positive-electrode terminal 7, and the negative-electrode terminal 8, the short-circuit in the weld flash of the sheathing film 6 etc. is prevented, and an adhesive property with the sheathing film 6, the positive-electrode terminal 7, and the negative-electrode terminal 8 improves.

[0045] In addition, in the gel electrolyte cell 1, the separator may be allotted into the gel electrolyte layer 4. The internal short circuit by contact to a positive electrode 2 and a negative electrode 3 can be prevented by allotting a separator into the gel electrolyte layer 4.

[0046] Moreover, although the case where the electrode winding object 5 which carries out the laminating of the band-like positive electrode 2 and the band-like negative electrode 3 through the gel electrolyte layer 4 as a gel electrolyte cell 1, and it comes to wind around a longitudinal direction further was used was mentioned as the example and the gestalt of operation mentioned above explained it This invention is not limited to this and can be applied also about the case where the winding path mold electrode object made into the so-called winding path, without winding is used when the laminating mold electrode object which comes to carry out the laminating of a positive electrode and the negative electrode through a gel electrolyte layer is used.

[0047] The gel electrolyte cell 1 concerning a gestalt of this operation which was

mentioned above is not limited especially about the configuration, and can make cylindrical, a square shape, etc. a thin shape and the various magnitude of large-sized **. Moreover, this invention is [primary cell] applicable also about a rechargeable battery. [0048]

[Example] The gel electrolyte cell of a configuration as mentioned above was produced that the effectiveness of this invention should be checked, and the example shown below estimated the property.

[0049] <Sample 1> First, it is the following, and the positive electrode was made and produced.

[0050] in order to produce a positive electrode, 5 % of the weight is first distributed [a cobalt acid lithium (LiCoO_2) / 92 % of the weight and powder polyvinylidene fluoride] for 3 % of the weight and a powder graphite to N-methyl pyrrolidone -- making -- a slurry-like positive electrode -- the mixture was prepared. next, this positive electrode -- the mixture was applied to homogeneity to both sides of the aluminium foil used as a positive-electrode charge collector, and the positive-active-material layer was formed by carrying out reduced pressure drying at 100 degrees C for 24 hours. And by carrying out pressing of this with a roll press machine, it considered as the positive-electrode sheet, and the positive-electrode sheet concerned was cut down to band-like [50mmx300mm], and it considered as the positive electrode. The lead made from aluminum was welded to the active material layer agensis part of a positive-electrode charge collector, and it considered as the positive-electrode terminal.

[0051] Next, it is the following, and the negative electrode was made and produced.

[0052] in order to produce a negative electrode, 9 % of the weight is first distributed [an artificial graphite] for 91 % of the weight and powder polyvinylidene fluoride to N-methyl pyrrolidone -- making -- a slurry-like negative electrode -- the mixture was prepared. next, this negative electrode -- the mixture was applied to homogeneity to both sides of the copper foil used as a negative-electrode charge collector, and the negative-electrode active material layer was formed by carrying out reduced pressure drying at 120 degrees C for 24 hours. And by carrying out pressing of this with a roll press machine, it considered as the negative-electrode sheet, and the negative-electrode sheet concerned was cut down to band-like [52mmx320mm], and it considered as the negative electrode. The lead made from nickel was welded to the active material layer agensis part of a negative-electrode charge collector, and it considered as the negative-electrode terminal.

[0053] And the gel electrolyte layer was formed on the positive electrode produced as mentioned above and the negative electrode. In order to have formed the gel electrolyte layer, first, hexafluoropropylene mixes and dissolved [agitated and] the polyvinylidene fluoride by which copolymerization was carried out, nonaqueous electrolyte, and dimethyl carbonate at 6.9% of a rate, and obtained the sol-like polyelectrolyte solution.

[0054] Here, nonaqueous electrolyte dissolved LiPF_6 in the mixed solvent with which it comes to mix ethylene carbonate (EC) and propylene carbonate (PC) at a rate of 6:4 at a rate of 0.85 mol/kg. Further 2 and a 4-difluoro anisole (DFA) were added at 1% of the weight of a rate, vinylene carbonate (VC) was added at 0.5% of the weight of a rate, and it prepared.

[0055] Next, the polyelectrolyte solution of the shape of an acquired sol was applied to homogeneity to both sides of a positive electrode and a negative electrode. Then, it was made to dry and the solvent was removed. Thus, the gel electrolyte layer was formed in

both sides of a positive electrode and a negative electrode.

[0056] Next, the laminating of the band-like positive electrode which was produced as mentioned above and with which the gel electrolyte layer was formed in both sides, and the band-like negative electrode with which the gel electrolyte layer was formed in both sides was carried out, it considered as the layered product, and the electrode winding object was acquired by winding this layered product around that longitudinal direction further.

[0057] It obturated, when aluminium foil sandwiched this winding object with the sheathing film into which it comes to be inserted with the resin film of a pair and finally carried out thermal melting arrival under reduced pressure of the periphery edge of a sheathing film, and the winding object was sealed in the sheathing film. In addition, at this time, the piece of resin was assigned to the positive-electrode terminal and the negative-electrode terminal, and the part concerned was put between the obturation section of a sheathing film. Thus, the gel electrolyte cell was completed.

[0058] <Sample 2> The gel electrolyte cell was completed like the sample 1 except the presentation of the nonaqueous electrolyte which constitutes a - <sample 69> sol-like electrolytic solution having been shown in Table 1 - 4.

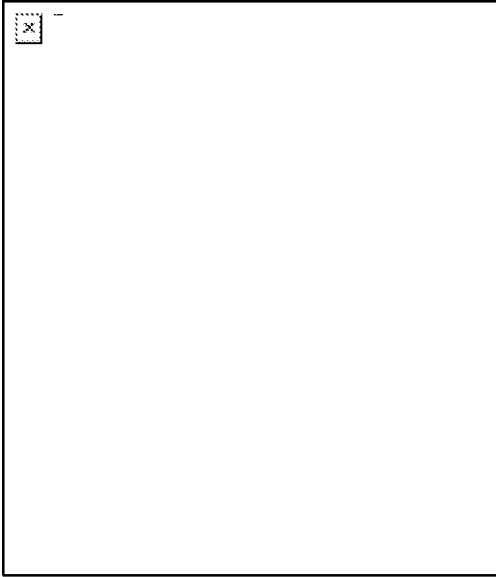
[0059] In addition, with the sample 40, the polyacrylonitrile and the poly methacrylonitrile were mixed and used as a matrix polymer. Molecular weight mixed the poly methacrylonitrile of 180,000, ethylene carbonate, propylene carbonate, and LiPF₆ with the polyacrylonitrile of 200,000 at a rate of 1:1:9:9:1.7 by the weight ratio, and molecular weight dissolved the polymer at 90 degrees C. This was applied on the electrode like the case of a sample 1, was annealed, and was made to gel. And the laminating of the band-like positive electrode and band-like negative electrode in which the gel electrolyte layer was formed was carried out through the separator which consists of porosity polyolefine, it considered as the layered product, and the electrode winding object was acquired by winding this layered product around that longitudinal direction further. This electrode winding object was sealed in the sheathing film like the sample 1.

[0060] Below, the solvent presentation of nonaqueous electrolyte and the addition concentration of vinylene carbonate are shown about a sample 1 - a sample 69. Moreover, in the case of different conditions from a sample 1, it also showed the electrode material, the electrolyte salt, etc. in front Naka. Especially when unstated, it was made to be the same as that of a sample 1.

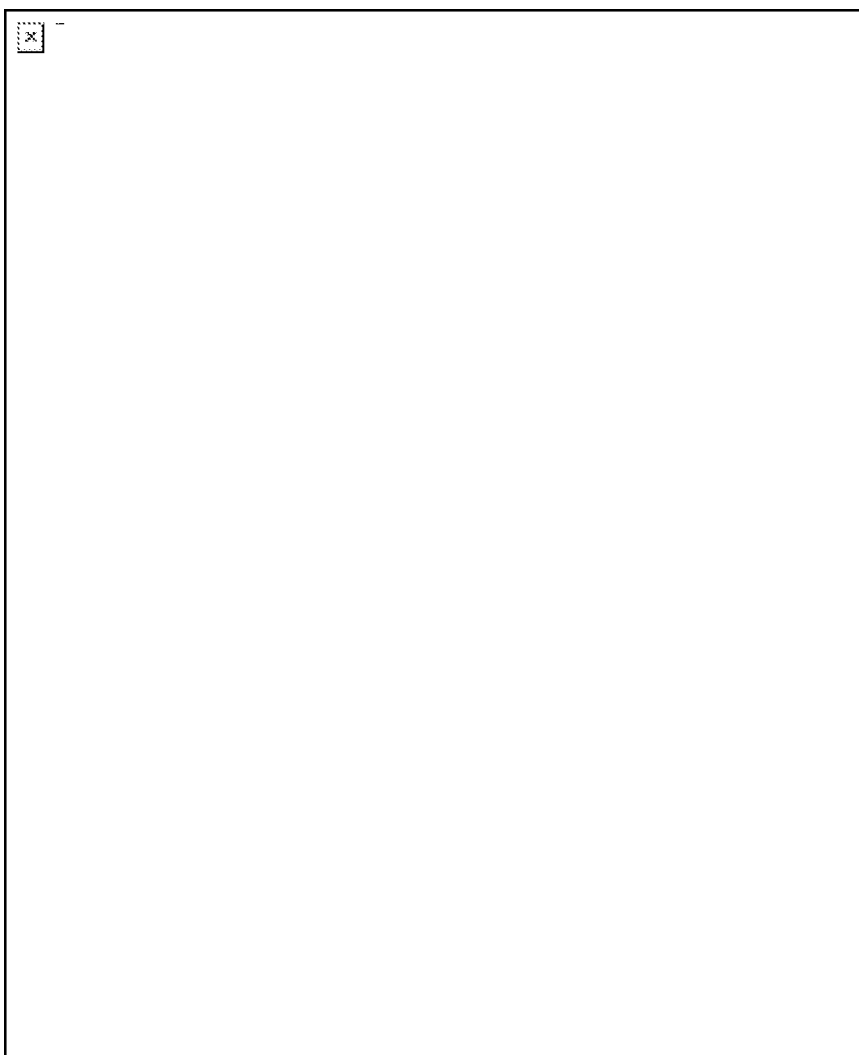
[0061] In addition, the nonaqueous electrolyte presentation of the cell in a sample 1 - a sample 15 is shown in Table 1 shown below. Moreover, the nonaqueous electrolyte presentation of the cell in a sample 16 - a sample 40 is shown in Table 2. Moreover, the nonaqueous electrolyte presentation of the cell in a sample 41 - a sample 54 is shown in Table 3. Moreover, the nonaqueous electrolyte presentation of the cell in a sample 55 - a sample 69 is shown in Table 4.

[0062]

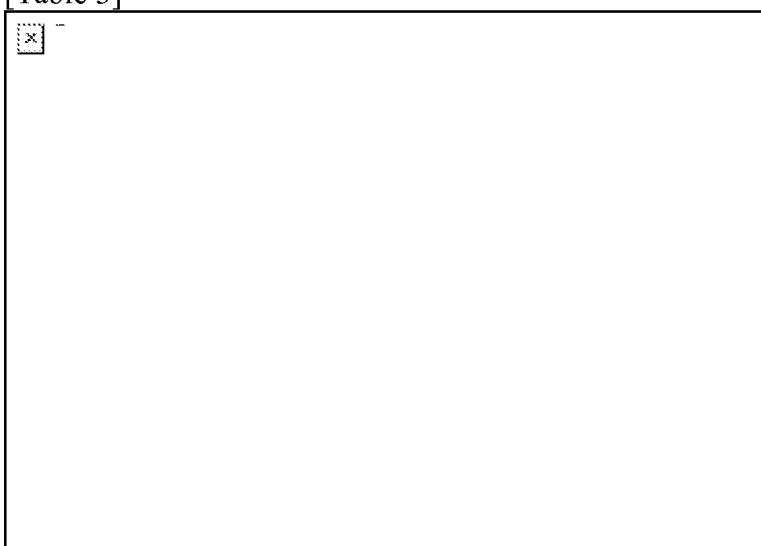
[Table 1]



[0063]
[Table 2]

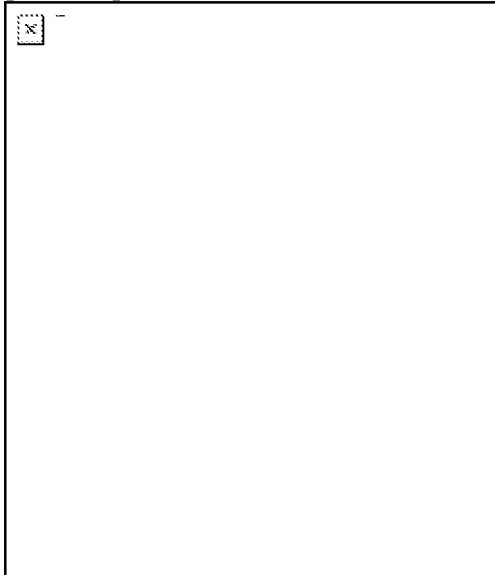


[0064]
[Table 3]



[0065]

[Table 4]



[0066] About the gel electrolyte cell of the sample 1 produced as mentioned above - a sample 69, a cycle property, first time charge-and-discharge effectiveness, the low-temperature discharge property, the load characteristic, and the property of first time discharge capacity were evaluated.

[0067] In addition, in the evaluation approach shown below, 1C is a current value which makes the rated capacity of a cell discharge in 1 hour, and is a current value which makes the rated capacity of a cell discharge in 5 hours, 2 hours, and 20 minutes, respectively in 0.2C, 0.5C, and 3C.

[0068] As a cycle property, constant current constant-potential charge of 4.2V and 1C and 3V cut-off constant-current discharge of 1C were performed, and the change for every cycle of discharge capacity was measured. Here, the capacity maintenance factor after 300 cycles examined, and 80% or more was made into good. It is the value by which the capacity maintenance factor is generally needed in the spec. of current and pocket electronic equipment 80% in 300 cycles.

[0069] (Discharge 300 Capacity of cycle eye)/(discharge capacity of 5 cycle eye)

As first time charge-and-discharge effectiveness, the first-time charge and discharge test was performed by the constant current constant-potential charge of 4.2V and 0.1C, 0.1C constant-current discharge, and cut-off 3V, and it evaluated from the cell capacity of the charge and discharge in that case. If this value is too small, the futility of the thrown-in active material will become large. 80% or more was made into good.

[0070] (First time discharge capacity)/(first time charge capacity)

As a low-temperature discharge property, the ratio of the 0.5C discharge capacity under a -20-degree C environment and the 0.5C discharge capacity under a 23-degree C environment estimated. The case where this value was 35% or more was made into good. This is equivalent to a cell capacity required to perform an emergency call once [at least] with a cellular phone etc. in the cold district around -20 degrees C.

[0071] (0.5C discharge capacity in -20 degrees C)/(0.5C discharge capacity in 23 degrees

C)

As a load characteristic, the ratio of the 3C discharge capacity and 0.5C discharge capacity in a room temperature estimated. The case where this value was 90% or more was made into good. In order that a cellular phone may consume power by the pulse discharge, the high current engine performance is required. 90% or more of value is a value required to fill the demand to a telephone.

[0072] $(3C \text{ discharge capacity}) / (0.5C \text{ discharge capacity})$

As a discharge capacity, first time discharge capacity estimated, and when there were 600 or more mAh from the design of a cell, it considered as good.

[0073] The characterization result of the cycle property about the gel electrolyte cell of a sample 1 - a sample 69, first time charge-and-discharge effectiveness, a low-temperature discharge property, a load characteristic, and first time discharge capacity is shown in Table 5 - 8.

[0074] In addition, the characterization result of the cell in a sample 1 - a sample 15 is shown in Table 5 shown below. Moreover, the characterization result of the cell in a sample 16 - a sample 40 is shown in Table 6. Moreover, the characterization result of the cell in a sample 41 - a sample 54 is shown in Table 7. Moreover, the characterization result of the cell in a sample 55 - a sample 69 is shown in Table 8.

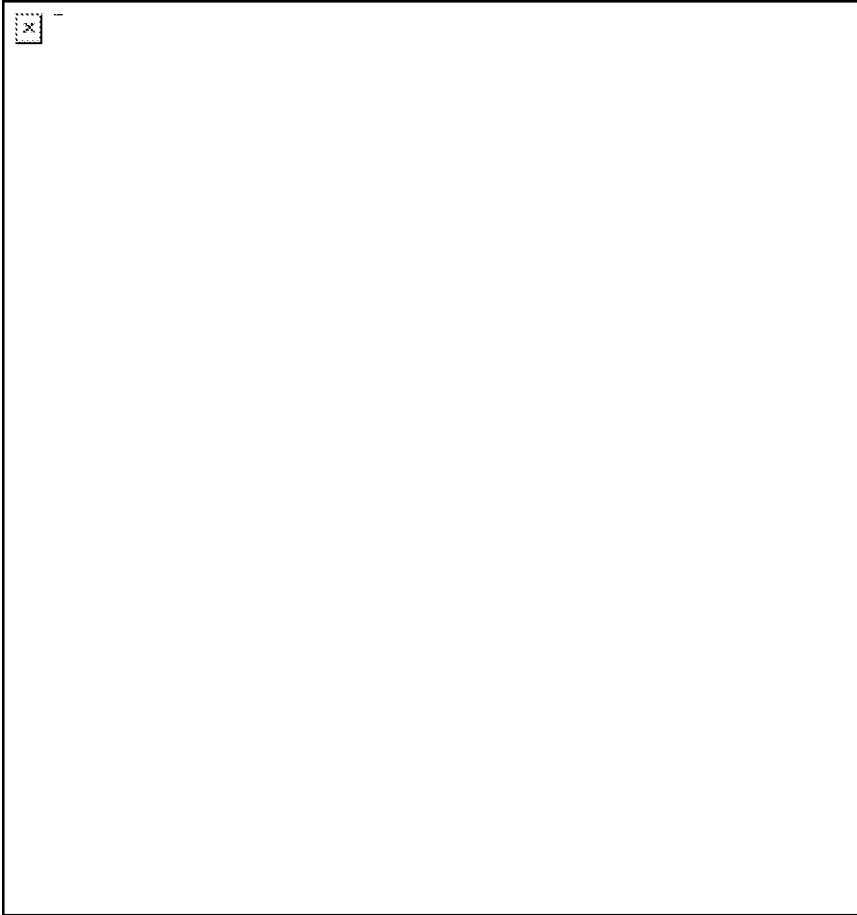
[0075]

[Table 5]

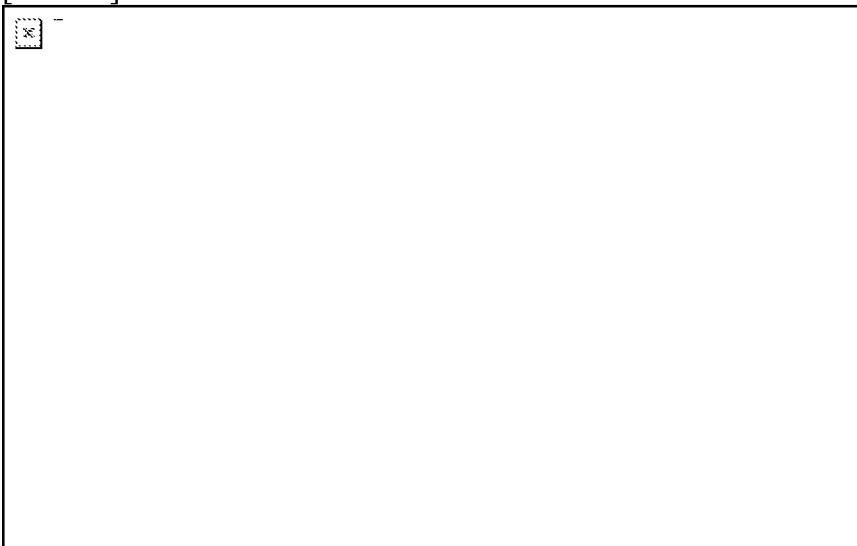


[0076]

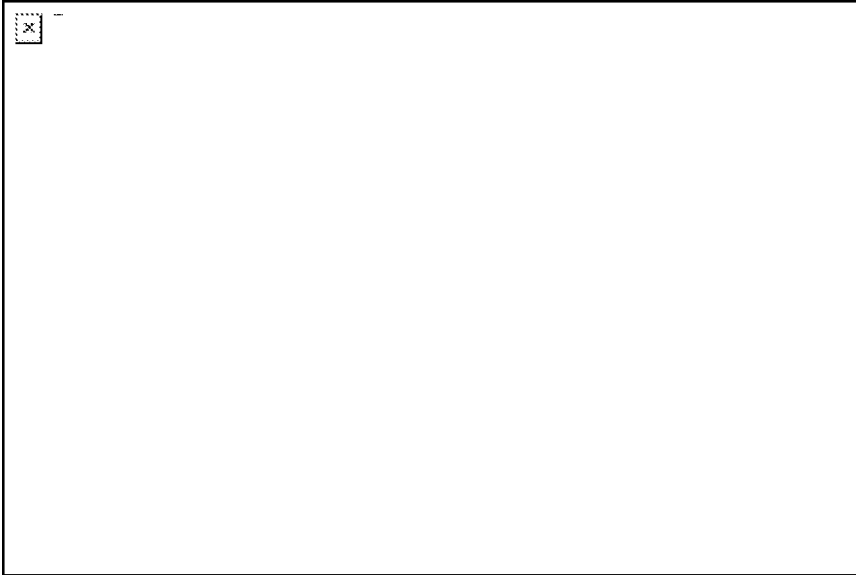
[Table 6]



[0077]
[Table 7]



[0078]
[Table 8]



[0079] In the gel electrolyte cell using the mixed solvent of ethylene carbonate and propylene carbonate, charge-and-discharge effectiveness and cell capacity can be greatly raised by adding vinylene carbonate in a gel electrolyte so that clearly from above Table 5 - 8. Furthermore, even if many propylene carbonate is included, a cycle property also improves.

[0080] Moreover, 0.05 % of the weight or more and 5% of the weight or less of the range and a good property are more preferably acquired for the addition of vinylene carbonate to the nonaqueous electrolyte in a gel electrolyte at the time of 0.5 % of the weight or more and 3% of the weight of the range.

[0081] If there are few additions of vinylene carbonate than 0.05 % of the weight, highly [the reinforcement of gel, and stability] enough, the effectiveness of raising charge-and-discharge effectiveness is not fully acquired, but neither a high cell capacity nor a cycle property is acquired. First time charge-and-discharge effectiveness and cell capacity improve greatly along with the increment in an addition of vinylene carbonate. Moreover, the effectiveness of bulging control of a cell also increases. However, if the addition of vinylene carbonate exceeds 5 % of the weight, a load characteristic will fall a little and a low-temperature property will fall greatly.

[0082] On the other hand, about the non-aqueous-solvent presentation of nonaqueous electrolyte, when it considers as the range of 15:85-75:25 by the weight ratio of ethylene carbonate and propylene carbonate, it turns out that the good property is shown. When a low-temperature property will be spoiled if there is too more ethylene carbonate than this, and there is too much propylene carbonate, first time charge-and-discharge effectiveness and cell capacity become less good.

[0083] Moreover, the good property is acquired when the lithium ion concentration to a non-aqueous solvent is the range of 0.4 or more mol/kg and 1.0 mol/kg as electrolyte salt concentration. When electrolyte salt concentration exceeds 1.0 mol/kg, a low-temperature property and a cycle property will be degraded. Moreover, sufficient capacity is not securable if electrolyte salt concentration is thinner than kg in 0.4 mols /. Moreover, a low-temperature property and cell capacity can be made good by using the salt of an imide system.

[0084] Moreover, it turns out that the charge-and-discharge effectiveness of a gel electrolyte cell can be raised further, and a high discharge capacity can be obtained by adding a difluoro anisole in nonaqueous electrolyte.

[0085] Moreover, the flatulence of the cell accompanying the generation of gas at the time of first time charge was also examined. The cell volume immediately after first time charge to the cell volume in front of charge boiled the flatulence of a cell comparatively, and it was evaluated more.

[0086] Consequently, by the cell of the sample 1 which added VC 0.5% of the weight - a sample 3, the cell volume immediately after the first time charge over just before charge was 103.9%. Moreover, by the cell of the sample 4 which added VC 1.0% of the weight - a sample 6, the cell volume immediately after the first time charge over just before charge was 103.6%. Moreover, by the cell of the sample 7 which added VC 2.0% of the weight - a sample 9, the cell volume immediately after the first time charge over just before charge was 101.3%. Moreover, by the cell of the sample 10 which added VC 3.0% of the weight - a sample 12, the cell volume immediately after the first time charge over just before charge was 100.6%. Moreover, by the cell of the sample 13 which added VC 5.0% of the weight - a sample 15, the cell volume immediately after the first time charge over just before charge was 100.1%. On the other hand, by the cell of the sample 55 which did not add VC - a sample 59, the cell volume immediately after the first time charge over just before charge was 109.8%.

[0087] As mentioned above, in the gel electrolyte cell using the mixed solvent of ethylene carbonate and propylene carbonate, even if many propylene carbonate is included by adding vinylene carbonate in a gel electrolyte, it turns out that the generation of gas by charge is suppressed and bulging of a cell can be prevented. Moreover, it turns out that the effectiveness is also so high that there are many additions of vinylene carbonate.

[0088] By the cell of the sample 60 added 6.0% of the weight - a sample 64, VC The cell volume immediately after the first time charge over just before charge is 100.0%, and VC by the cell of the sample 65 added 7.0% of the weight - a sample 69 The cell volume immediately after the first time charge over just before charge is 100.0%, and if there are too many amounts of vinylene carbonate as it mentioned above from a viewpoint of bulging control of a cell, although the way with many amounts of vinylene carbonate was desirable, a load characteristic and a low-temperature property will fall.

[0089]

[Effect of the Invention] Since vinylene carbonate or its derivative is added, the gel electrolyte of this invention can raise the chemical stability of a gel electrolyte and a negative electrode.

[0090] And the gel electrolyte cell of this invention using the gel electrolyte excellent in such chemical stability, reinforcement, and solution retention turns into an outstanding cell on which cell capacity, the cycle property, the load characteristic, and the low-temperature property were satisfied. Thus, the gel electrolyte cell of this invention which realized the outstanding engine performance contributes to development of the industry in connection with pocket mold electronic equipment greatly.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the perspective view showing the example of 1 configuration of the gel electrolyte cell of this invention.

[Drawing 2] It is the perspective view showing the condition that an electrode winding object is held into a sheathing film.

[Drawing 3] It is a sectional view in an A-B line among drawing 2 .

[Description of Notations]

1 Gel Electrolyte Cell 2 Positive Electrode 3 Negative Electrode 4 Gel Electrolyte Layer,
5 Electrode Winding Object 6 Sheathing Film 7 Positive-Electrode Terminal 8 Negative-
Electrode Terminal Piece of 9 Resin
